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► **To cite this version:**

Leifeng Zhang, Bertrand Radiguet, Patrick Todeschini, Christophe Domain, Yang Shen, et al.. Investigation of solute segregation behavior using a correlative EBSD/TKD/APT methodology in a 16MND5 weld. *Journal of Nuclear Materials*, 2019, 523, pp.434-443. 10.1016/j.jnucmat.2019.06.002 . hal-02172714

HAL Id: hal-02172714

<https://normandie-univ.hal.science/hal-02172714>

Submitted on 25 Oct 2021

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1 **Investigation of solute segregation behavior using a correlative**

2 **EBSD/TKD/APT methodology in a 16MND5 weld**

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8

9 **Abstract**

10 In the present study, a correlative Electron Backscattering Diffraction
11 (EBSD)/Transmission Kikuchi Diffraction (TKD)/Atom Probe Tomography (APT)
12 methodology was used to investigate the solute segregation behavior in a low-alloyed weld.
13 Three dimensional chemical information was correlated to the crystallographic features of
14 Grain Boundaries (GBs). The steel has a complex microstructure of acicular ferrite and
15 intergranular carbides. About 78% High Angle Grain Boundaries (HAGBs, with about 12%
16 $\Sigma 3$ HAGBs) and about 22% Low Angle Grain Boundaries (LAGBs) were observed. APT
17 analyses revealed the segregation of one element or several chemical species (C, P, Mn, Si, Ni,
18 Cr and Mo) at GBs or carbide-ferrite interfaces. Taking into account the nature of segregants
19 and the five-parameter GB crystallography, both interstitial and substitutional segregation
20 behaviors were discussed. The results reveal a significant influence of misorientation angle
21 (or deviation angle) on interstitial segregation for LAGBs (or $\Sigma 3$ special HAGBs) and also a

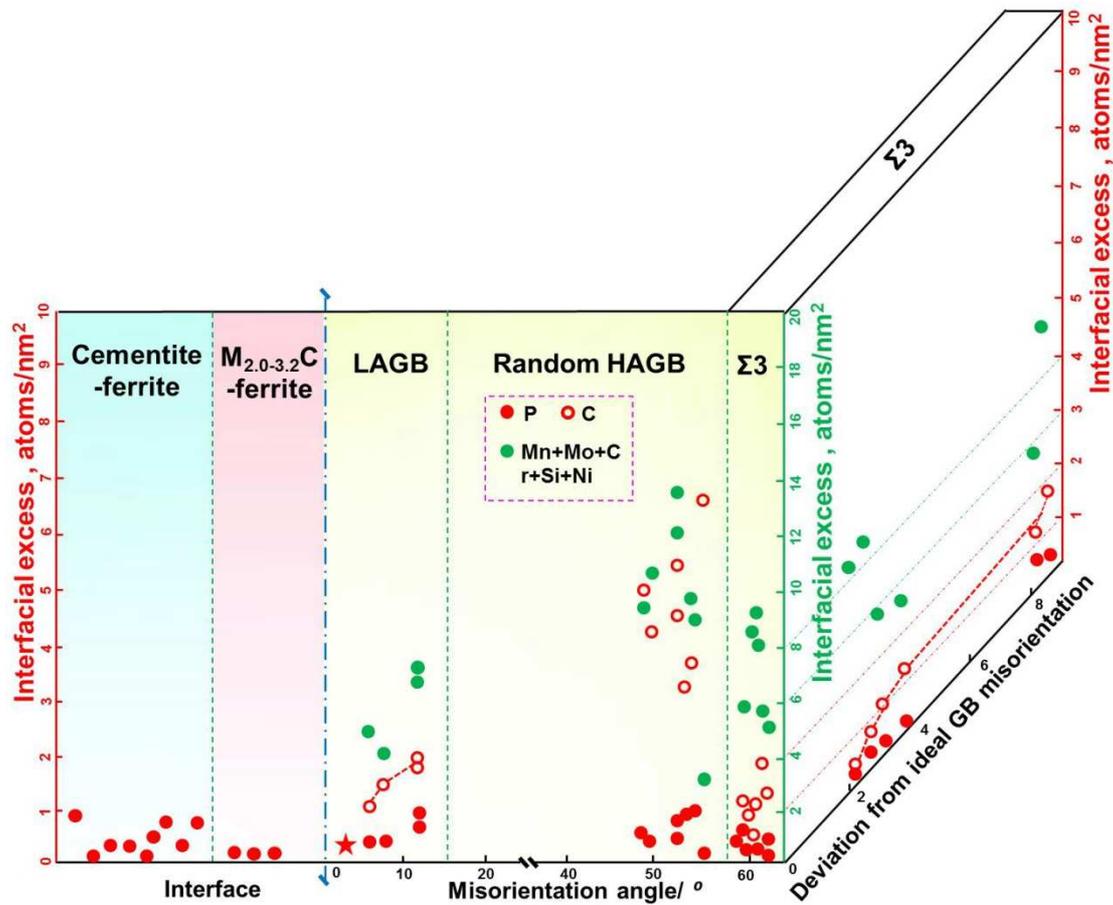
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22 strong influence of the GB plane on substitutional segregation for $\Sigma 3$ special HAGBs and
23 general HAGBs.

24 **Key words:** Grain boundaries; interfaces; APT; segregation; acicular ferrite; carbide

25 **Graphical abstract**



26

27 1. Introduction

28 Solute segregation to GBs may be either beneficial or detrimental for properties [1]. For the
29 past 60 years, GB segregation issue in Reactor Pressure Vessel (RPV) steels and other alloys,
30 in particular the intergranular P segregation, has been intensively studied both experimentally
31 and by modelling as reviewed in literature [2-9]. Experimental research is frequently carried
32 out by Auger Electron Spectroscopy (AES) that requires GBs to be fractured. Analyses are
33 performed on selected “brittle” GBs with a high segregation level [10-13]. AES has a fast
34 acquisition speed to collect the data and a good precision on the composition measurement,

35 but the crystallographic information is lost. Later, a new door has been opened with some
36 advanced techniques, including Analytical Electron Microscopy (AEM) [14, 15] and Atom
37 Probe Field Ion Microscopy (APFIM) [16, 17]. These tools allow a precise measurement of
38 the chemical segregation at the atomic level to be obtained even for non-brittle alloying
39 systems. Transmission Electron Microscopy-Energy Dispersive Spectrometry (TEM-EDS)
40 can provide both crystallographic and chemical information. However, TEM is confined to 2
41 dimensions, the depth information being difficult to be determined. Electron Energy Loss
42 Spectroscopy (EELS) can provide a wealth of information (for example, concentration,
43 nearest-neighbor atomic structure, local thickness and free-electron density), but the
44 convolution of all the detected information in a single spectrum makes it challenging to
45 quantify absolute values [18]. In contrast, APT is a unique technique in quantifying local
46 chemical composition, offering extensive capabilities for both 3D mapping at fine scale and
47 chemical composition measurements at the atomic scale (atomic resolution in depth and 0.3-
48 1.0 nm laterally) [19]. Particularly, it has strong ability to identify multiple chemical species
49 in one sample with high sensitivity, and its acquisition efficiency as well as detection capacity
50 has been improved [20]. Today, the crystallographic details, as provided by electron
51 microscopies (including TEM [21], EBSD and/or TKD [22-28]), can be correlated to APT
52 data. This has been reviewed in the literature [29].

53 The improvement of these instruments or the correlative methodologies helps to perform
54 in-depth investigations of GB segregation behavior. As reported in a nanocrystalline material,
55 a correlative TEM/APT approach has established a clear C segregation map in relation with
56 GB misorientation angle [21, 30]. The C segregation level increases with the misorientation
57 angle in the LAGB region. In contrast, there exists a large data scattering in the HAGB region,
58 in which the same misorientation angle may correspond to both high and low segregation

59 levels. For polycrystalline materials with a complex composition, the detailed solute
60 segregation behavior in relation with GB nature was rarely reported.

61 This paper focuses on a 16MND5 weld, which is produced for RPV, a component acting as
62 a barrier between the primary water and the reactor building. With the intensive expectations
63 for extending the service lifespans of Nuclear Power Plants (NPPs), it is of more and more
64 importance to get a reliable evaluation of the microstructural change and the corresponding
65 property degradation of RPV steels [31]. The RPV steels, subjected to thermal ageing and
66 neutron irradiation, may embrittle gradually during operation [32]. This embrittlement is
67 mainly attributed to a hardening mechanism, related to the formation of Cu-rich [33, 34] and
68 Ni, Mn, Si-rich features [35-37]. These features can pin the dislocations and reduce their
69 mobility, thus enhancing the yield strength. Besides, a non-hardening mechanism, due to
70 intergranular impurity segregation (especially P) that impairs the GB cohesion, could also
71 contribute to the embrittlement [7, 38]. For VVER-1000 RPV welds being exposed at 310-
72 320°C up to 200000 h, the reversible temper brittleness due to the intergranular P
73 accumulation was responsible for thermal ageing effects and a considerable increase of
74 intergranular embrittlement tendency [4]. APT analyses on VVER-1000 base and weld metals
75 revealed an obvious GB segregation of P (and also other alloying elements), but no detailed
76 information on GB features was given [39]. The co-segregation behavior of P and other
77 alloying elements has also been reported in Cr-Mo(-V) steels [40-42]. However, the detailed
78 segregation behavior for all chemical species, especially that with regard to the GB character,
79 remains unclear.

80 The main aim of this research is to quantify GB segregation in a 16MND5 weld steel.
81 Using the correlative EDS/TKD/APT methodology [24, 26, 43], the crystallographic
82 information, or the 5 Degrees of Freedom (DOFs), and chemical composition were collected
83 simultaneously. Both the interstitial and substitutional segregations were discussed. The

84 segregation behavior at carbide-ferrite heterophase boundaries was also studied.

85 **2. Experimental method**

86 **2.1 Material, sample preparation and experimental conditions**

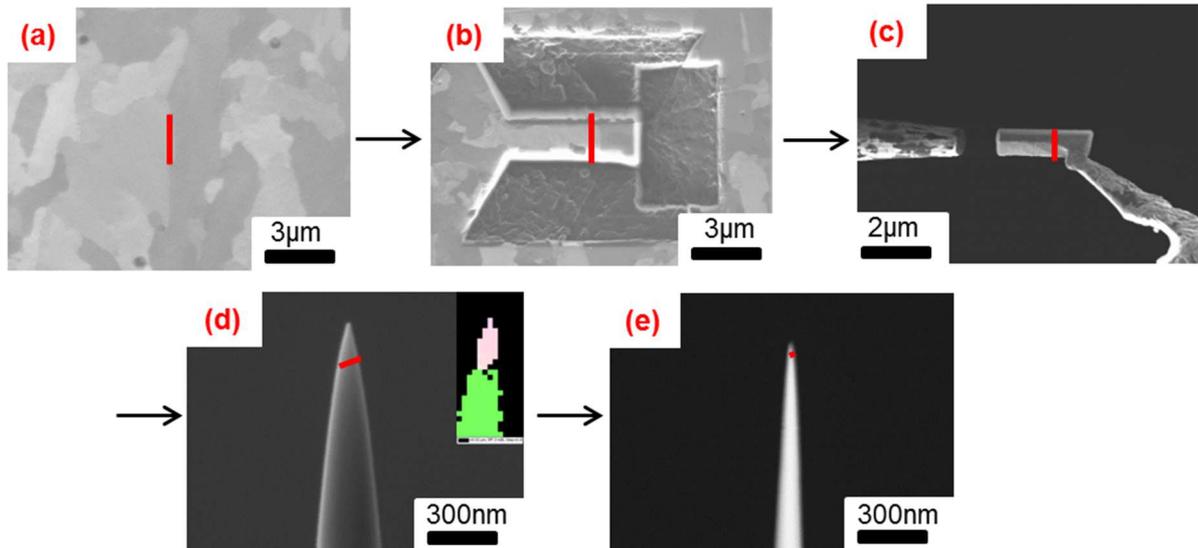
87 The chemical composition of the 16MND5 weld steel is listed in Table 1. The P content is
88 80 wt.ppm (or 140 at.ppm). After steelmaking, forging and welding (submerged arc welding),
89 the subsequent stress-relief heat treatment was performed at 595-610°C for 16.5 h, followed
90 by a controlled cooling at 15°C/h down to 350°C and then air cooling to ambient temperature.
91 The microstructure was observed by Scanning Electron Microscopy (SEM) and EBSD in a
92 dual-beam SEM/FIB instrument (Zeiss Nvision 40 with the AZtec acquisition software and
93 XB 540 with the TEAM-EDAX software). Specimens for SEM/EBSD analyses, in the shape
94 of thin slices of 10×10×0.3 mm³, were cut from as-received half Charpy sample and then
95 fixed into a conductive resin with a diameter of 25 mm. Afterwards, the specimens were
96 ground with coarse, medium and fine sandpaper discs and then polished on special cloths with
97 diamond liquids. The samples were finally polished in a semi-automatic polishing machine
98 for 30 min using a 0.04 μm colloidal silica suspension. Samples for SEM observations were
99 finally chemically etched with 1% Nital solution for 60 s. The EBSD experiments were
100 performed at 20 kV at a working distance of 10 mm, with a step size of 0.1 μm×0.1 μm.
101 Patterns were captured with a 4×4 binning mode on the DigiView 5 camera from EDAX. For
102 statistics, any point pair with misorientation exceeding 2° was regarded as a boundary. Based
103 on Coincidence Site Lattice (CSL) theory in cubic lattice, the GBs, with misorientation
104 characteristics of 60°⟨111⟩ considering a tolerance of 8.7° were considered as Σ3 special
105 HAGBs [5]. The tolerance value is defined by K/Σ^n , where K is a constant, Σ value is
106 calculated by the ratio between all sites and coincident sites at the boundary plane. The
107 angular tolerance value is defined according to Brandon Criterion [44], selecting a K value of
108 15 and a n value of 0.5.

109

Table 1 Bulk chemical composition of the 16MND5 weld steel

| | C | P | Si | Mn | Ni | Cr | Mo | Cu | Fe |
|--------------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| wt. % | 0.07 | 0.008 | 0.43 | 1.57 | 0.75 | 0.16 | 0.58 | 0.04 | Bal. |
| at. % | 0.34 | 0.014 | 0.84 | 1.60 | 0.72 | 0.18 | 0.34 | 0.04 | Bal. |

110 Fig. 1 depicts the experimental sequence for the detailed site-specific sample preparation,
111 starting from the GB identification in bulk material to the final APT tip, at the apex of which a
112 specific GB was located. In Fig. 1a, after selecting a GB, FIB was utilized to mill trenches
113 (Fig. 1b). As shown in Fig. 1c, a micromanipulator and a Gas Injection System (GIS) were
114 used to lift out the wedge-shaped chunk containing the Region of Interest (ROI), which was
115 subsequently placed on the cap of tungsten pre-tip. During the subsequent annular milling
116 (Fig. 1d), FIB column was used as a milling tool to sharpen the tip at 30 kV, with the beam
117 currents decreasing successively from 700 pA to 40-50 pA. To minimize the Gallium-
118 contaminated layer in the tip, the final cleaning procedure was completed at 2 kV with a
119 current of 100 pA. To ensure the specific GB being located near the apex of the final tip (Fig.
120 1e), TKD was used during the final steps of annular milling. This is because the imaging
121 contrast in SEM view failed to identify the GB location when the tip was too thin (<300-500
122 nm). In contrast, TKD technique can help to locate the GB's position during annular milling.
123 The second advantage of using TKD is to obtain the 5 DOFs with the combination of APT 3D
124 reconstruction. The HKL channel 5 software (or the TSL-OIM software) and Carine
125 crystallography software were utilized for the identification of GB crystallography. It should
126 be noticed that, for the GB plane identification, the maximum Miller index values are limited
127 to 6 in these softwares.



128

129 **Fig. 1** Steps of sample preparation of an APT needle containing a GB: (a) selection of a ROI
 130 containing a specific GB; (b) milling a slice with FIB; (c) lift-out the chunk with a micromanipulator;
 131 (d) annular milling with TKD; (e) cleaning with FIB. Note that, the GB location is delineated by a
 132 solid red line and in (d), the TKD image showing the distinct contrasts across a GB is placed at the
 133 top right area.

134 Microanalyses were carried out with a Local Electrode Atom Probe (LEAP 4000 XHR,
 135 CAMECA) operated at a temperature of 55 K, a detection rate of 0.15%, a pulse repetition
 136 rate of 200 kHz and a pulse fraction equal to 20% of the standing voltage. It was reported that
 137 some light-weight elements (such as B [45], P [46] and C [47]) may migrate from one place to
 138 another (particularly low-index poles) along the tip surface prior to field evaporation. In that
 139 case, the observed atomic position in the reconstructed volume may not correspond to the
 140 original location in the steel. The enhanced surface migration could be of particular concern
 141 for the laser-pulsed mode atom probe where heating effect is more favored [48, 49]. That is
 142 why a high-voltage pulse mode was adopted in the present research. The 3D reconstruction
 143 procedure for APT data analyses has been stated in relevant literature [50-52]. According to
 144 these principles and the visible crystallographic poles from the detector event histogram map,
 145 the image compression factor and field factor were determined. Both the commercial IVAS
 146 software (CAMECA, v. 3.6.6) and the GPM 3D software (from GPM lab, v. 6.3) were used
 147 for data reconstruction.

148 2.2 Data analyses for GB chemistry and crystallography

149 2.2.1 Identification of crystallographic detail

150 Five independent parameters (or 5 DOFs) are required to fully describe the structure of a
151 GB between grains A and B. Three DOFs, including one for misorientation angle θ and two
152 for rotation axis $\mathbf{c} = [h_0k_0l_0]$, are used to define the mutual misorientation between the two
153 crystals, and two DOFs are applied to depict the GB planes $(h_{nA}k_{nA}l_{nA})/(h_{nB}k_{nB}l_{nB})$. Thus,
154 a GB can be expressed by: $\theta^\circ[h_0k_0l_0](h_{nA}k_{nA}l_{nA})/(h_{nB}k_{nB}l_{nB})$. The orientation of grain A
155 can be displayed by a third-order matrix (\mathbf{g}_A), in which its tri-axial orientation projections
156 are: $\mathbf{X}_A = (r_{A11}, r_{A12}, r_{A13})$, $\mathbf{Y}_A = (r_{A21}, r_{A22}, r_{A23})$ and $\mathbf{Z}_A = (r_{A31}, r_{A32}, r_{A33})$. Those for
157 crystal B, in a third-order matrix (\mathbf{g}_B), can be expressed as: $\mathbf{X}_B = (r_{B11}, r_{B12}, r_{B13})$, $\mathbf{Y}_B =$
158 $(r_{B21}, r_{B22}, r_{B23})$ and $\mathbf{Z}_B = (r_{B31}, r_{B32}, r_{B33})$. As exhibited in Fig. 2a, the mutual misorientation
159 relationship is virtually a rotation matrix, \mathbf{R}_{AB} , which can be expressed as follows [53]:

$$160 \quad \mathbf{R}_{AB} = \mathbf{g}_B \cdot \mathbf{g}_A^{-1} = \begin{pmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{pmatrix}$$

161 In fact, \mathbf{R}_{AB} depicts the rotation of a grain along a specific crystallographic direction,
162 yielding the rotation angle (θ)/axis (\mathbf{c}) pair. The smallest rotation angle between the two grains
163 is the misorientation angle (or disorientation angle) [28, 54]. And the θ/c pair can be deduced
164 as below [54]:

$$165 \quad \theta = \cos^{-1} \left[\frac{1}{2} (r_{11} + r_{22} + r_{33} - 1) \right]$$

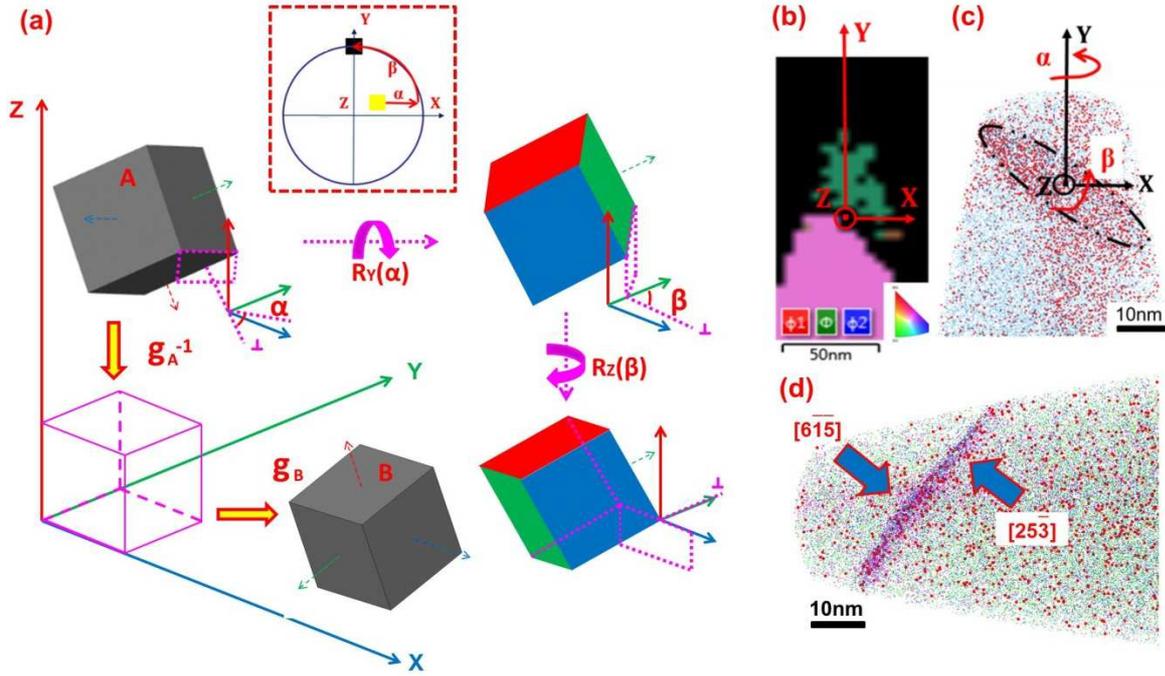
$$166 \quad \mathbf{c} = [c_1, c_2, c_3] = \frac{1}{2\sin\theta} (r_{32} - r_{23}, r_{13} - r_{31}, r_{21} - r_{12})$$

167 After acquiring the TKD image (Fig. 2b), the θ/c pair can be calculated by the software. To
168 recognize the GB planes, both the TKD information and the 3D data reconstruction
169 information need to be combined. Next, an example is applied to illustrate the detailed

170 procedures for identifying the two GB planes with Carine crystallography software.

171 A crystal of grain A (\mathbf{g}_A) is created here. And the stereographic projection map is plotted
172 along \mathbf{Z}_A axis (as illustrated in Fig. 2a in local coordinate system). Then, two rotations are
173 applied to bring the GB plane perpendicular to the Y axis. The two rotation angles, α and β ,
174 from which the GB plane normal can be aligned with Y axis, are identified by the
175 combination of the TKD map (Fig. 2b) and the APT atom map (Fig. 2c). The two maps are
176 originally placed at the coincidental position. The atom map is rotated along Y axis until the
177 GB projection appears like a straight line (referred to Fig. 2d) in X-Y plane, and α is the
178 corresponding rotation angle. To obtain β , the atom map is rotated a second time until this
179 straight-line GB projection is perpendicular to the Y axis.

180 After doing this, the GB normal direction of grain A is identified as $(\overline{615})$ for grain A. By
181 creating a crystal similar to grain B (\mathbf{g}_B) and performing the similar operation, the GB plane
182 of grain B is identified to be $(\overline{253})$. Besides, the schematic illustrations of α and β , as well as
183 the detailed rotation procedures for crystal A, are depicted in Fig. 2a. The TKD analysis from
184 Fig. 2b gives a misorientation information of $52^\circ[\overline{101}]$. Thus, this general HAGB can be
185 expressed as: $52^\circ[\overline{101}](\overline{615})/(\overline{253})$. The identification process has also been described in [43].



186

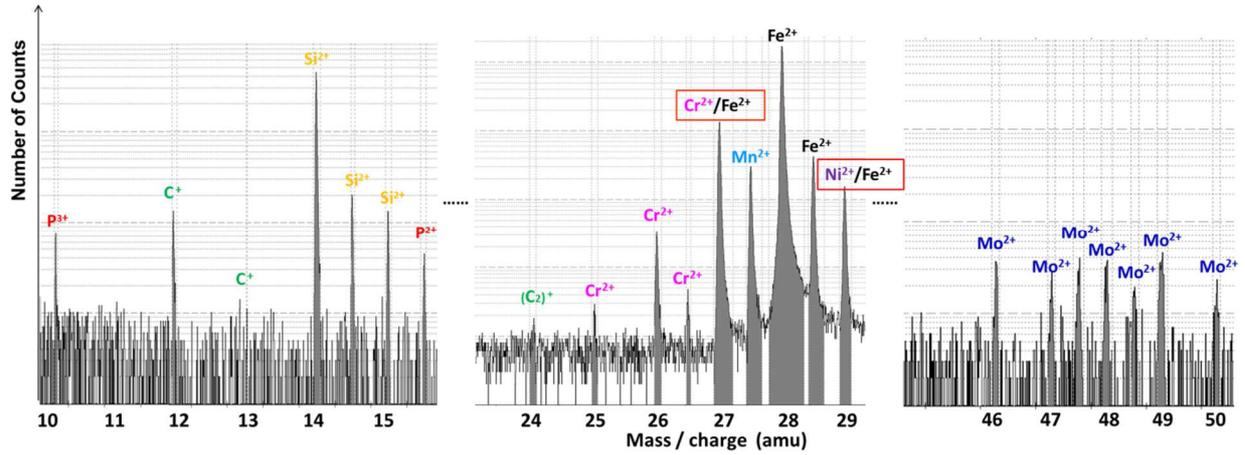
187 Fig. 2 Schematic illustrations revealing the mutual misorientation (between grain A and grain B) and
 188 the identification of GB plane for grains A and B: (a) the mutual misorientation (between the two
 189 crystals) and the two rotations ($R_Y(\alpha)$ - the rotation along Y axis by α and $R_Z(\beta)$ - the rotation along Z
 190 axis by β , operated in their local coordinate systems) for identifying the GB plane normal direction of
 191 grain A; (b) the TKD map exhibiting the GB misorientation information; (c) the reconstructed 3D
 192 map with the two rotations (α and β); (d) the GB plane normal directions relative to grains A and B.
 193 In (a), “ \perp ” represents the GB plane normal direction, and the tri-axial orientations of grain A are
 194 illustrated by arrows with different colors (X axis in red, Y axis in green and Z axis in blue). In the
 195 stereographic projection map, the GB plane direction is illustrated by the yellow square dot, and the
 196 final special direction, perpendicular to Y axis, is marked by black square dot.

197 **2.2.2 Calculation of the GB interfacial excess**

198 In Fig. 3, some detected ions after APT analyses are exhibited in a partial mass spectrum.
 199 The total concentration of an element is calculated from the proportion of detected ions after
 200 identifying each isotope and removing the background information. The uncertainty of the
 201 measured concentration of element i , if considering only the statistical variation, is given by:

202
$$\sigma_i = \sqrt{\frac{X_i(1-X_i)}{N_{at}}}$$

203 where X_i is the measured concentration of solute i and N_{at} is the total number of atoms in the
 204 analyzed volume.



205

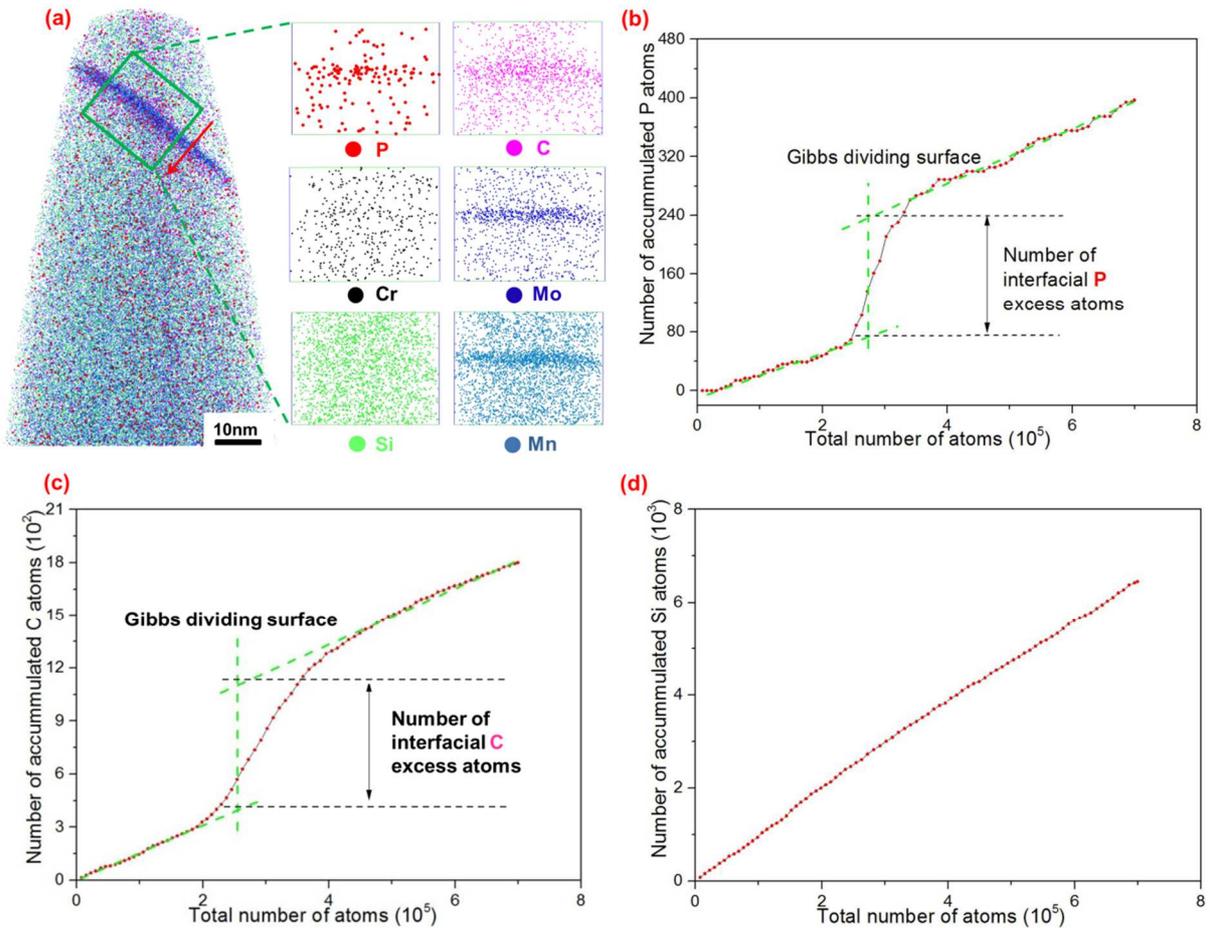
206 **Fig. 3 A partial mass spectrum showing the peak-noise level of some isotopes in ferrite matrix**

207 As shown in Fig. 4a, the GB is visible on the 3D reconstruction map owing to an obvious
 208 enrichment of C, P, Mn, Mo and Cr. A sampling cylinder perpendicular to the GB is then
 209 selected to plot cumulative profile through the GB. Fig. 4b, c & d plot the cumulative profiles
 210 of P, C and Si, respectively. A general method based on the Gibbsian interfacial excess Γ_i [55]
 211 was adopted. The Γ_i value (in atoms/nm²) is defined as:

212

$$\Gamma_i = \frac{N_i^{\text{excess}}}{\eta \cdot A}$$

213 in which N_i^{excess} is the number of atoms in excess determined from cumulative profile, η is
 214 the detection efficiency of the LEAP and A is the interfacial area of the selected volume. In
 215 comparison to C and P, nearly no Si segregation was detected at this GB. Taking into account
 216 the uncertainty of each element, the error bar can be measured.



217

218 **Fig. 4** APT data analyses for: (a) the selected volume (Φ 21.6 \times 16.6 nm³) exhibiting the element
 219 distribution perpendicular across a general HAGB; (b)-(d) the cumulative profiles (corresponding to
 220 16.6 nm) of calculated atoms across the HAGB for P, C and Si elements.

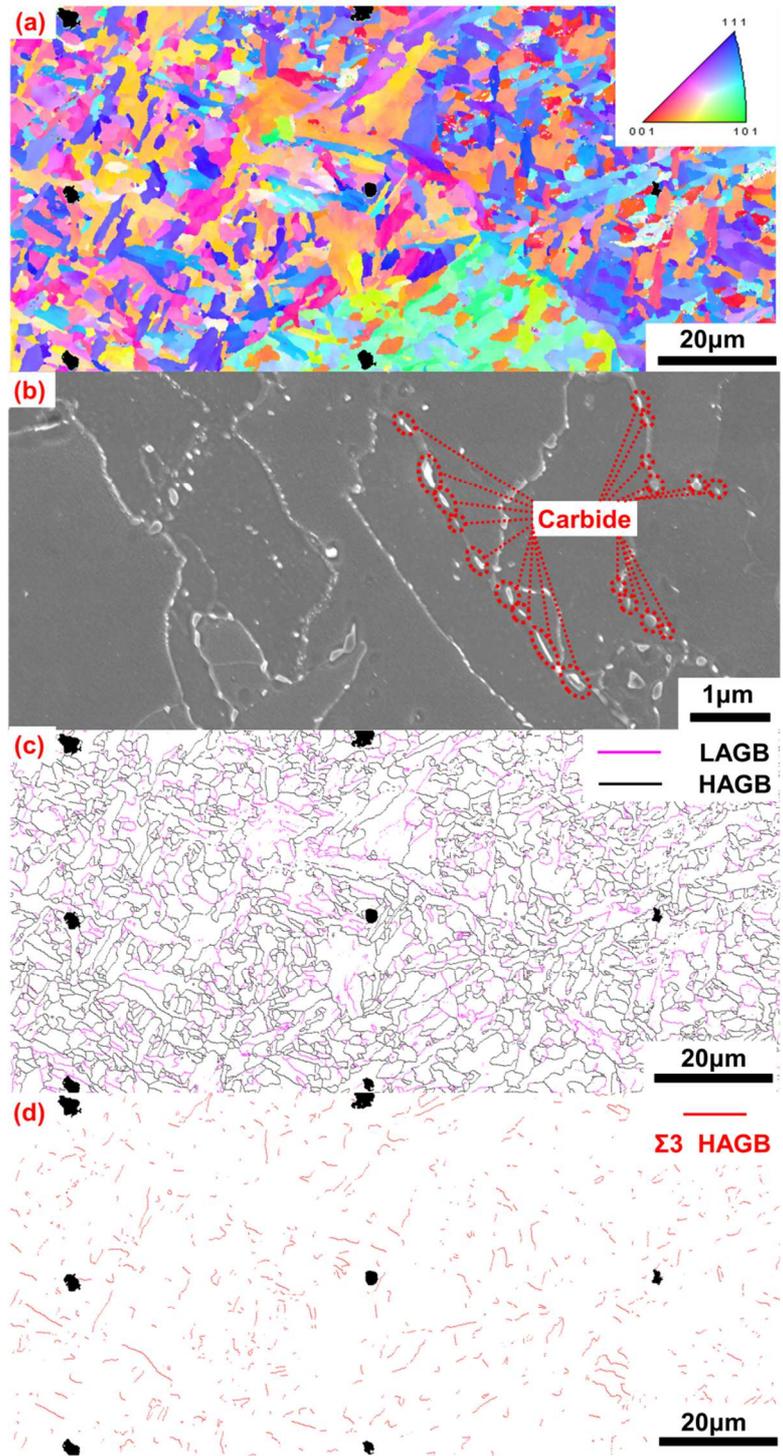
221 3. Results

222 3.1 Microstructure characterization and GB identification

223 The microstructure of the 16MND5 weld is exhibited in Fig. 5a. The inverse pole figure
 224 reveals numerous acicular ferrite grains with distinct orientations. These thin grains are
 225 arranged in an irregular way, i.e., they intersect with each other. Compared with the “sheaf-
 226 like” bainitic ferrite, the acicular ferrite has a “basket-weave” morphology [56]. Similar to
 227 bainitic phase transformation, the orientation relationships between parent austenite and
 228 acicular ferrite variants are also Nishiyama-Wassermann (N-W) and Kurdjumov-Sachs (K-S)
 229 [57]. Numerous carbides are present along the GBs, as shown in Fig. 5b. These carbides have
 230 a nanometer size with various shapes: spherical, ellipsoidal, rod-like and plate-like. Two types

231 of carbides, characterized by extensive APT analyses, have the stoichiometry of M_3C (where
232 M consists of Fe, Mn, Mo and Cr [58]) and $M_{2.0-3.2}C$ (where M contains Fe, Mo and Cr). The
233 Fe concentration is higher than 50 at.% in M_3C carbides (or cementite), while in $M_{2.0-3.2}C$
234 carbides, Mo concentration is over 35 at.% and the Fe concentration is less than 30 at.%.
235 Thus, the weld metal mainly has a complex microstructure of acicular ferrite and intergranular
236 carbides (without any intragranular carbides being detected).

237 LAGB & HAGB is one classification of GB species, in which GBs with a misorientation
238 angle larger than 15° are considered as HAGBs. As exhibited in Fig. 5c, the proportion of
239 HAGB is about 78%, and that of LAGB is about 22%. Among HAGBs, some special ones
240 ($\Sigma 3$, $\Sigma 5$, $\Sigma 7$...) are included. The $\Sigma 3$ HAGBs are the most favored ones according to the phase
241 transformation orientation relationship [57]. In Fig. 5d, $\Sigma 3$ special HAGBs represent about
242 12% of total HAGBs. Due to the presence of numerous carbides, carbide-matrix interfaces are
243 of critical importance. The boundaries are classified as GBs (~22% LAGBs, ~66% general
244 HAGBs and ~12% $\Sigma 3$ HAGBs) and carbide-ferrite interfaces.



245

246 Fig. 5 Characterization of the microstructure and the corresponding GBs: (a) Inverse pole figure
 247 map; (b) SEM image showing the intergranular carbides; (c) HAGBs & LAGBs; (d) $\Sigma 3$ HAGBs.
 248 Note that, the 9 black marks are created regularly by FIB milling as complementary signals to
 249 identify the relative location of different grains.

250 **3.2 Intergranular segregation and carbide-ferrite interfacial segregation**

251 Table 2 lists the calculated interfacial excess values of identified GBs and interfaces for

252 several chemical species (C, P, Si, Mn, Ni, Cr and Mo). It is inferred that all the LAGBs,
 253 general HAGBs, $\Sigma 3$ HAGBs and carbide-matrix interfaces provide effective sites for the
 254 segregation of several elements (P, C, Si, Mn, Ni, Cr and Mo). The segregated P contents are
 255 relatively low for all the $\Sigma 3$ HAGBs and all the $M_{2.0-3.2}C$ carbide-ferrite interfaces. No
 256 depletion of any chemical species was detected.

257 **Table 2 Interfacial excess values (in atoms/nm²) of the segregated elements for the GBs and interfaces**

| Element | P | C | Si | Mn | Ni | Cr | Mo |
|--|-----------|---------|-----------|---------|---------|---------------|---------|
| LAGB 5°[652](503)/(320) | 0.3±0.2 | 1.1±0.4 | 0.28±0.05 | 2.9±0.2 | 0.8±0.4 | 0.20±0.0 4 | 1.0±0.3 |
| LAGB 7°[011](434)/(656) | 0.3±0.2 | 1.3±0.4 | 0.38±0.06 | 2.1±0.1 | 0.8±0.2 | - | - |
| LAGB 12°[104](546)/(535) | 0.9±0.3 | 1.8±0.9 | 0.5±0.1 | 4.8±0.5 | 1.5±0.8 | - | 0.6±0.4 |
| LAGB 12°[310](631)/(631) | 0.5±0.2 | 2.0±0.7 | 0.30±0.04 | 4.0±0.2 | 1.4±0.7 | - | 0.9±0.3 |
| $\Sigma 3$ HAGB 59°[111](652)/(503) | 0.2±0.1 | 0.4±0.1 | 1.3±0.2 | 4.1±0.3 | 2.3±0.3 | - | 0.4±0.2 |
| $\Sigma 3$ HAGB 60°[111](112)/(310) | 0.2±0.1 | 1.0±0.6 | 0.5±0.2 | 3.2±0.3 | 1.4±0.7 | 0.2±0.1 | 0.5±0.3 |
| $\Sigma 3$ HAGB 60°[343](441)/(415) | 0.3±0.2 | 1.8±0.6 | 2.1±0.3 | 5.3±0.4 | 1.3±0.3 | - | 0.6±0.4 |
| $\Sigma 3$ HAGB 59.5°[111](411)/(522) | 0.3±0.2 | 0.8±0.6 | 1.4±0.2 | 6.5±0.7 | - | - | 0.3±0.2 |
| $\Sigma 3$ HAGB 60°[111](101)/(011) | 0.07±0.06 | 1.2±0.4 | 0.34±0.03 | 3.5±0.1 | 0.5±0.3 | 0.4±0.1 | 0.7±0.2 |
| $\Sigma 3$ HAGB 60°[443](451)/(103) | 0.4±0.2 | 1.2±0.6 | 0.8±0.1 | 4.0±0.2 | 0.8±0.4 | 0.2±0.1 | 0.6±0.2 |
| General HAGB 52°[101](615)/(253) | 0.4±0.2 | 4.6±1.2 | - | 6.5±0.4 | 2.0±0.5 | 0.3±0.1 | 3.4±1.5 |
| General HAGB 49°[403](010)/(355) | 0.6±0.3 | 5.0±1.2 | 0.5±0.1 | 5.8±0.3 | 1.1±0.5 | 0.3±0.1 | 1.8±0.9 |
| General HAGB 49.5°[110](425)/(542) | 0.3±0.1 | 4.1±1.4 | 1.3±0.2 | 7.1±0.4 | - | 0.5±0.2 | 1.7±0.9 |
| General HAGB 54°[243](110)/(150) | 1.0±0.5 | 3.7±1.0 | 0.8±0.1 | 5.6±0.5 | 0.8±0.4 | - | 1.4±1.0 |
| General HAGB 52°[331](543)/(655) | 0.8±0.2 | 5.3±1.1 | 1.9±0.2 | 6.6±0.3 | 1.8±0.9 | 0.4±0.1 | 2.8±1.0 |
| General HAGB 54°[525](112)(031) | 0.11±0.02 | 6.7±1.6 | - | 1.7±0.1 | - | 0.4±0.1 | 1.5±0.4 |
| General HAGB 54°[433](552)/(631) | 0.9±0.3 | 3.3±0.9 | 0.54±0.07 | 4.8±0.3 | 1.7±1.0 | 0.3±0.1 | 2.7±0.7 |
| Cementite-ferrite Interface 1 | 0.8±0.4 | - | 0.9±0.4 | - | 0.8±0.1 | - | - |

| | | | | | | | |
|---|-----------|---|-----------|---------|---------|---|---|
| Cementite-ferrite Interface 2 | 0.06±0.05 | - | - | - | - | - | - |
| Cementite-ferrite Interface 3 | 0.2±0.1 | - | - | - | - | - | - |
| Cementite-ferrite Interface 4 | 0.2±0.1 | - | - | - | - | - | - |
| Cementite-ferrite Interface 5 | 0.03±0.02 | - | 2.8±0.5 | - | - | - | - |
| Cementite-ferrite Interface 6 | 0.4±0.2 | - | - | - | 0.3±0.1 | - | - |
| Cementite-ferrite Interface 7 | 0.7±0.2 | - | - | - | - | - | - |
| Cementite-ferrite Interface 8 | 0.2±0.1 | - | - | - | 0.6±0.3 | - | - |
| Cementite-ferrite Interface 9 | 0.8±0.3 | - | - | - | 0.6±0.3 | - | - |
| M _{2.0-3.2} C carbide-ferrite Interface 1 | 0.2±0.1 | - | 0.38±0.01 | 4.0±0.2 | - | - | - |
| M _{2.0-3.2} C carbide-ferrite Interface 2 | 0.10±0.04 | - | 1.7±0.1 | 5.5±0.2 | 1.6±0.8 | - | - |
| M _{2.0-3.2} C carbide-ferrite Interface 3 | 0.14±0.09 | - | 0.3±0.1 | 2.0±0.2 | 0.6±0.3 | - | - |

258 Notes: “-” means that no obvious segregation or depletion is detected.

259 The peak and average values of P interfacial excess for each GB and interface types are
260 listed in Table 3. The average values of segregated P contents are higher in LAGBs and
261 general HAGBs than in other boundary types. The variation of the segregated P content from
262 one carbide-ferrite interface to another could be attributed to their distinct lattice coherencies
263 between carbide and ferrite matrix.

264 **Table 3 Interfacial excess values (in atoms/nm²) of P for the identified boundaries. For each type of GB or**
265 **interface, the number of investigated features is given into parenthesis.**

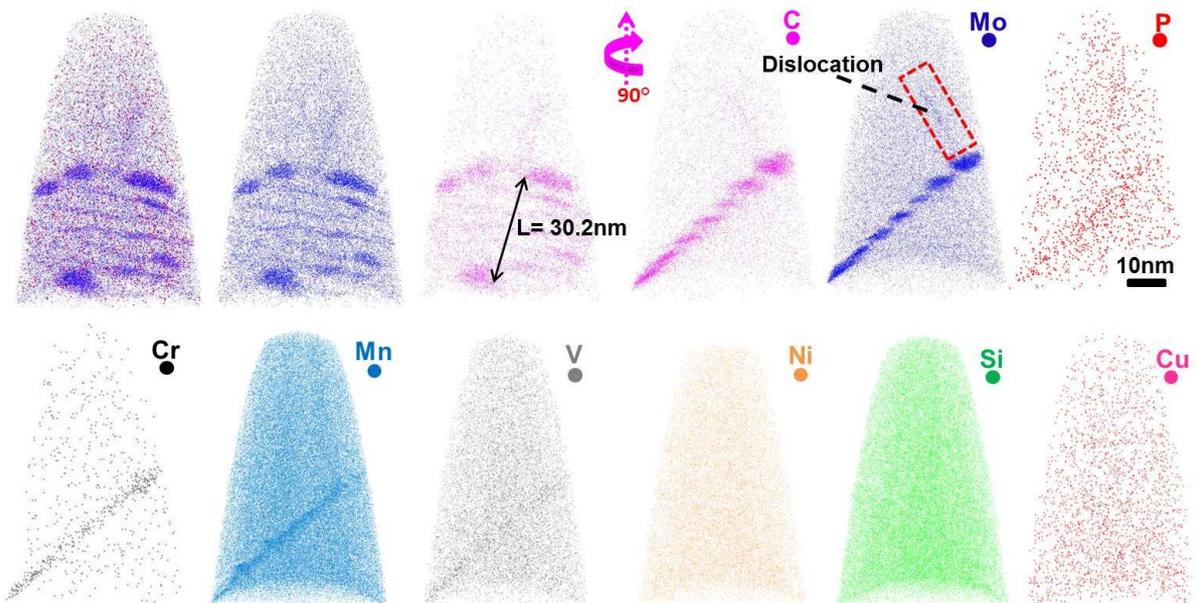
| | GBs | | | Interfaces | |
|----------------|--------------|----------------------|-----------------|-------------------------------------|--|
| | LAGBs (4) | General HAGBs (7) | Σ3 HAGBs (6) | Cementite-ferrite interfaces (9) | M _{2.0-3.2} C carbide-ferrite interfaces (3) |
| Peak | 0.9±0.3 | 1.0±0.5 | 0.4±0.2 | 0.8±0.4 (or 0.8±0.3) | 0.2±0.1 |
| Average | 0.5±0.2 | 0.6±0.2 | 0.2±0.1 | 0.4±0.2 | 0.15±0.07 |

266

267 As exhibited in Fig. 6, another LAGB $3^\circ[\bar{5}\bar{2}3](5\bar{4}\bar{3})/(3\bar{3}4)$ was also investigated (not
268 reported in Table 2 & 3). It is clear that this tilted LAGB is composed of an array of parallel
269 accommodation edge dislocations. These dislocation lines are easily identified because of the
270 segregation of several elements (C, Mo, P, Cr, Mn and V). Similar observations were reported

271 in neutron-irradiated Fe-Cr model alloys [59, 60]. The Burgers vector was measured using the
 272 expression [5]: $|\mathbf{b}_{\text{exp}}| = 2 \cdot d \cdot \sin(\theta/2) \approx d \cdot \sin\theta$, where d is the distance between two
 273 intrinsic dislocations measured from the 3D reconstruction map ($d = (5.0 \pm 0.2)$ nm) and θ is
 274 the misorientation angle acquired from the TKD map ($\theta = 3^\circ$). In this case, $|\mathbf{b}_{\text{exp}}|$ was found to
 275 be (0.26 ± 0.01) nm. In BCC iron, the theoretical value of Burgers vector is given by $|\mathbf{b}_{\text{the}}| =$
 276 $\sqrt{3}/2$ a. With $a = 0.286$ nm (lattice parameter), $|\mathbf{b}_{\text{the}}|$ is about 0.25 nm, in excellent agreement
 277 with $|\mathbf{b}_{\text{exp}}|$ value. Some Mo, Cr, V and C-enriched features appear along these edge
 278 dislocations. For this LAGB, the solute segregation was not quantified and thus not reported
 279 in Table 2 & 3 because of the presence of some Mo, Cr, V and C-enriched features.

280 Besides, a dislocation with a clear Mo and C segregation also appears near the LAGB
 281 (shown in Fig. 6). In contrast, the P segregation is not so obvious. It seems that, in the
 282 16MND5 weld, P segregation at dislocations is not as obvious as that at GBs or carbide-ferrite
 283 interfaces.



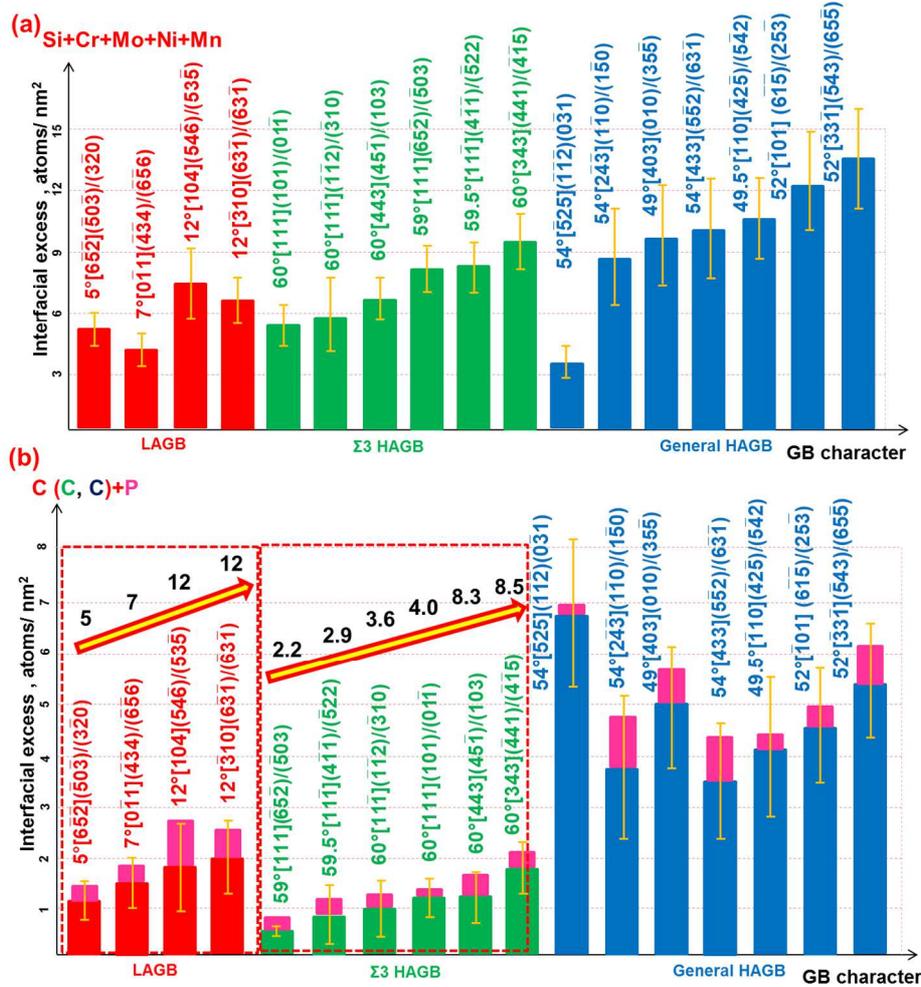
284

285 **Fig. 6** 3D reconstruction of a LAGB $3^\circ[\overline{523}](\overline{543})/(\overline{334})$ with a dislocation present near it. The tilted
 286 LAGB is composed of some primary edge dislocations spaced at an average distance $d = L/6 =$
 287 (5.0 ± 0.2) nm. The dislocation near the LAGB is delineated.

288 3.3 Interstitial segregation and substitutional segregation

289 The segregation level at a GB is correlated with both its Gibbs free energy and structure.
290 The GB with higher free energy promotes stronger segregation. For the present steel with a
291 multicomponent composition system, the intergranular segregation from all chemical species
292 is considered in a comprehensive way to clarify the GB segregation anisotropy with regard to
293 the 5 parameters of a GB.

294 It is acknowledged that Si, Cr, Mo, Ni and Mn favor substitutional segregation while C
295 enhances interstitial segregation. The calculated values of total interfacial excess values of
296 substitutional elements (Si, Cr, Mo, Ni and Mn) are plotted in Fig. 7a. It appears that the
297 segregated level of total substitutional elements is higher in general HAGBs than in LAGBs
298 or $\Sigma 3$ HAGBs. The average values for LAGBs, $\Sigma 3$ HAGBs and general HAGBs are (5.8 ± 1.3) ,
299 (7.2 ± 1.1) and (9.7 ± 1.9) atoms/nm², respectively. In practical steels, a $\Sigma 3$ HAGB possesses a
300 specific deviation angle from an ideal $\Sigma 3$ HAGBs, thus favoring a considerable segregation of
301 several elements. The substitutional segregation level of $\Sigma 3$ HAGBs is quite high, which
302 makes these $\Sigma 3$ HAGBs not real special from an energetic perspective. The substitutional
303 segregation level of $\Sigma 3$ HAGB $60^\circ[343](\bar{4}41)/(\bar{4}\bar{1}5)$, with a deviation angle of 8.5° , seems to
304 be competitive with that of a random HAGB.



305

306 **Fig. 7** Variation of total interfacial excess values with GB type for: (a) substitutional segregation
 307 (Si+Cr+Mo+Ni+Mn); (b) interstitial segregation of C (+ P, in black). Note that, different GB
 308 types are marked with distinct colors. Particularly, the values of misorientation angles for
 309 LAGBs, as well as the deviation angles for Σ 3 HAGB, are marked in b along the arrow plotting
 310 the increasing trend.

311 There is a variation of the total interfacial excess values among Σ 3 HAGBs and among
 312 general HAGBs. Probably, besides the Σ value, other factors are also responsible for the
 313 substitutional segregation behavior. In the present study, this variation could be explained by
 314 an influence of the two adjoining GB planes. It seems that if the GB plane has low Miller-
 315 index values, the segregation level will be low. This is the case in the Σ 3 HAGBs
 316 $60^\circ[111](101)/(01\bar{1})$ and $60^\circ[11\bar{1}](\bar{1}\bar{1}2)/(\bar{3}10)$ among all the Σ 3 HAGBs, and the case in the
 317 general HAGB $54^\circ[\bar{5}25](\bar{1}\bar{1}\bar{2})(0\bar{3}1)$ among all the general HAGBs. It is reported that the low

318 Miller-index GB planes tend to possess low energy [10, 61, 62]. When the adjoining two GB
319 planes tend to own high Miller-index values, the segregation level will be high. This rule,
320 consistent with previous experimental results [10], perfectly matches our observations for
321 substitutional segregation. Recent research on an AISI 304L stainless steel [63] also reported
322 that its corrosion behavior is dominated by GB plane for low- Σ CSL GBs and random
323 HAGBs. A possible explanation for the GB plane influence lies in the presence of large excess
324 volume for HAGBs with a high Miller-index value [64, 65]. The GB excess volume describes
325 the expansion ability induced by the presence of a GB in polycrystalline materials based on
326 hard sphere model [66]. A low Miller-index GB plane was reported to be associated with low-
327 energy and small amount of volume expansion in BCC metals [67].

328 As shown in Fig. 7b (if not taking into consideration the black bar representative of P), the
329 interfacial excess values of C are higher in all the general HAGBs than those in the LAGBs or
330 $\Sigma 3$ HAGBs. The segregated C content in all the $\Sigma 3$ HAGBs is much lower in comparison to
331 all general HAGBs, which renders $\Sigma 3$ HAGBs quite special with low energy. Moreover, the
332 segregated C content among LAGBs (or $\Sigma 3$ HAGBs) varies with the misorientation angle (or
333 the deviation angle). With the increased dislocation density, the segregated C content
334 increases with misorientation angle in the range 5-12°. For LAGBs with a misorientation of
335 12° ($12^\circ[104](54\bar{6})/(53\bar{5})$ and $12^\circ[\bar{3}10](6\bar{3}\bar{1})/(\bar{6}3\bar{1})$), the interfacial excess values of P and C
336 can go up to 0.9 ± 0.3 and 2.0 ± 0.7 atoms/nm², respectively. Similarly, the C segregation level
337 rises gradually with the increase of deviation angle in the range 2.2-8.5° (shown in Fig. 6b).

338 Notably, the segregation mechanism of P may be more complex. Density Functional Theory
339 (DFT) calculations (at 0 K) in α -Fe revealed that the segregation energy for a P atom placed in
340 substitutional position is lower than that in its interstitial position. According to this, some
341 research argued that some Fe atoms are substituted by P atoms at a GB [68-70]. Also, it was
342 predicted that P segregates interstitially at high temperature based on the enthalpy-entropy

343 compensation effect [71, 72]. Recently, Pavel Lejček revisited the data based on
344 thermodynamic calculations and proposed that, with the increase of temperature, there should
345 be an alteration of P segregation position at a GB in α -Fe: at 0 K, substitutional segregation of
346 P is preferred, while interstitial segregation occurs at high temperature (exceeding about 650
347 K). For practical interest (with a temperature above 700 K), the interstitial segregation of P is
348 explained by entropy driven transition of the segregation site [73]. According to this, the
349 probable segregation position of P is interstitial in the present steel.

350 If we consider (C+P) as interstitial segregants, it seems that the cumulative segregation
351 profile (for C+P as shown in Fig. 7b) does not change a lot, and that the cumulative
352 segregation level increases with misorientation angle (or deviation angle). It is reported that
353 there is a possible site competition between C and P, in which C atoms preferentially occupy
354 the sites at the GB, leaving less free sites for P segregation [8, 41, 74]. There is a much higher
355 segregation level for C than P for all GB types. Here, P is not separated individually
356 considering the potential site competition with C. To make a pertinent conclusion that P
357 segregates interstitially at high temperature, it is better to investigate a controlled composition
358 system with high-P but low-C to limit the segregated C content.

359 Though, in the current analysis, both P and C prefer interstitial segregation at GBs, they
360 bring in opposite effects. P is deleterious for mechanical property with particular weakening
361 effect on the cohesive strength between crystalline grains, while intergranular C decoration is
362 generally believed to be positive on GB cohesion [75, 76]. The C segregation at GBs
363 suppresses the intergranular fracture induced by P segregation, and this could be explained by:
364 (i) the enhanced GB cohesion by segregated C as its inherent effect [77] and (ii) the reduced P
365 segregation in association with the site competition mechanism that C atoms can replace the P
366 atoms at GBs [8].

367 We interpret the whole GB crystallography as well as the segregants in a comprehensive

368 way. In general, both the interstitial and substitutional segregation levels are high for the
369 random HAGBs (except the case $54^\circ[\bar{5}25](\bar{1}\bar{1}\bar{2})(0\bar{3}1)$). Among all the general HAGBs (or $\Sigma 3$
370 HAGBs), the variation of substitutional segregation level can be explained by the GB planes,
371 as discussed above. Typically, a GB with a misorientation angle smaller than 15° is considered
372 as a LAGB. According to the Frank-Bilby theory, a LAGB can be regarded as an array of
373 dislocations and the increase of misorientation angle can be released by the enhanced
374 dislocation density as well as the increased energy [78]. The increasing trend of interstitial
375 segregation level with misorientation angle (or deviation angle) in LAGBs (or $\Sigma 3$ HAGBs) is
376 also clear.

377 **4. Conclusions**

378 1) For the present research, a joint chemical characterization and crystallographic
379 identification were acquired on the same sample at the same location in a 16MND5 weld, and
380 the intergranular segregation behaviors were correlated to the 5 parameters. This correlative
381 EBSD/TKD/APT methodology opens a feasible way to quantify the GB segregation with
382 regard to its 5-parameter crystallography for polycrystalline materials with a complex
383 composition system.

384 2) The microstructure of the steel is mainly composed of acicular ferrite and intergranular
385 carbides. Two types of carbides, cementite carbide and $M_{2.0-3.2}C$ carbide, were detected in the
386 present steel. The typical boundaries in the experimental weld metal are classified as GBs and
387 carbide-ferrite interfaces. A classification of the GBs is $\sim 22\%$ LAGBs, $\sim 66\%$ random HAGBs
388 and $\sim 12\%$ $\Sigma 3$ HAGBs, and the carbide-ferrite interfaces include cementite-ferrite interfaces
389 and $M_{2.0-3.2}C$ carbide-ferrite interfaces.

390 3) There is an obvious segregation of one element or several chemical species (C, P, Mn,
391 Mo, Cr, Si and Ni) for all boundary types. The general HAGBs possess a high segregation
392 level for both interstitial and substitutional elements. Among all the general HAGBs (or $\Sigma 3$

393 HAGBs), there could be a significant influence of the two adjoining GB planes on
394 substitutional segregation. If a GB has two low Miller-index planes, the segregation level is
395 found to be low; and vice versa.

396 4) Interstitial segregation level increases with misorientation angle for LAGBs, and it also
397 increases with deviation angle for $\Sigma 3$ HAGBs. P, as well as C, is thought to favor interstitial
398 segregation. The average values of segregated P contents are higher in LAGBs and general
399 HAGBs than in other GB types or interfaces. Besides, the carbide-ferrite interfaces provide
400 effective sites for P segregation. It seems that P segregation at dislocations is not as obvious as
401 that at GBs or carbide-ferrite interfaces.

402 **Acknowledgement**

403 This work was performed on the GENESIS platform, financially supported by Centre National de la
404 Recherche Scientifique (CNRS) belonging to the project entitled “Investissements d’avenir” with a
405 reference number ANR-11-EQPX-0020. This work is part of the EM2VM Joint Laboratory Study and
406 Modeling of the Microstructure for Ageing of Materials. This work was supported by the MAI-sn
407 (Materials Ageing Institute-Scientific Network (<http://thema.org/scientific-network>)).

408 The authors also owe their sincere gratitude to Prof. Didier Blavette for the fruitful discussions.

409 **Research Data**

410 Data not available / Data will be made available on request.

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